



## A reusable polymer supported copper catalyst for the C–N and C–O bond cross-coupling reaction of aryl halides as well as arylboronic acids

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### ABSTRACT

A simple and industrially viable protocol for C–N and C–O coupling was reported here. The polymer supported heterogeneous copper catalyst was prepared from chloromethyl polystyrene using a simple procedure. O-Arylation of substituted phenols with various aryl halides was achieved using this copper catalyst in DMSO medium. This heterogeneous copper catalyst, also efficiently works for the N-arylation of N–H heterocycles with arylboronic acids in methanol. This catalyst was also effective in amination reaction of primary amines with aryl halides as well as arylboronic acids in DMSO medium. The effects of solvent, base and temperature for the O-Arylation and amination reactions were reported. Further, the catalyst can be easily recovered quantitatively by simple filtration and reused up to several times without sufficient loss of its catalytic activity.

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### 1. Introduction

The formation of aryl-nitrogen and aryl-oxygen bonds via cross-coupling reactions represent a powerful means for the preparation of various compounds that are of biological, pharmaceutical and material interest [1–3]. The development of a mild and highly efficient method for synthesis of N-arylazoles over classical Ullmann type [4], or nucleophilic aromatic substitution reactions [5], or coupling with organometallic reagents [6,7] has recently gained considerable attention in synthetic chemistry [8]. Due to the economic attractiveness of copper [9] and by using some special ligands such as N,N- and N, O-bidentate compounds, many Cu-catalyzed C–N [10,11], C–O [12,13], C–S [14,15], and C–C [16,17] bond formation reactions have led to a resurgence of interest in carbon-heteroatom coupling reactions, and their applications seem to be of more and more importance [18,19]. The copper-mediated Ullmann coupling reaction [20,21] is still the straightforward method to form the requisite carbon-heteroatom bonds. However, the synthetic scope of this reaction is strongly limited by the insolubility of copper(I) salts in organic solvents, the high reaction temperatures required (200 °C) and the sensitivity of the

substituted aryl halide to the harsh reaction conditions applied. Another major drawback of this protocol is the use of stoichiometric amounts of copper or copper salts, which results in the production of large quantities of waste, making this method environmentally unfriendly. Milder reactions using transmetallating agents, such as triarylboranes [22], aryl lead triacetates [7], arylboronic acids [23,24] and hypervalent aryl siloxanes [6] have been developed but these alternatives are limited since the preparation of highly functionalized substrates usually requires multistep sequences. Despite significant progress in the Cu-catalyzed N/O-arylation reaction, only a few reports have appeared describing the couplings of imidazoles and/or phenols with arylboronic acids/aryl bromides or of functional substrates or of hindered substrates [25,26] without the recovery of catalyst. Therefore, it is important to develop more simple and efficient catalytic systems for the cross-coupling methodology with an ability to utilize arylboronic acids/aryl bromides [27,28] with reusability of catalyst. By using certain copper precatalysts and ligands, successful N-arylation of anilines [29,30], amides [31], hydrazides [32], oxazolidinones [33] and various N–H heterocycles [34] with aryl halides as arylating reagents was reported. However, only limited papers have contributed to N-arylation of alkylamines (not chelating substrates) and various N–H heterocycles in heterogeneous condition [35,36]. To date, few reports described reusable copper catalytic systems for this C–O coupling that allowed the recycling of active metal,

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nevertheless only some reported leaching measurements of metal toxic residues in final products [37,38].

Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse. These disadvantages can be overcome by anchoring metal on suitable supports which will allow easy separation and recyclability of the catalyst with minimal amount of product contamination with metal. These studies confirm that the anchoring of metal on solid support not only exhibits improved catalyst activity, stability and selectivity of the product but also enables easy recovery and reuse of the catalyst.

Herein we report the synthesis of a polymer supported copper catalyst and illustrate its application in a number of cross-coupling reactions such as *O*-arylation, *N*-arylation and amination reactions. Our strategy was to attach a ligand to a polymer support and then allow it to bind to copper through ligand exchange. The resulting binding interaction also needs to be strong enough to prevent the copper from dissociating from the polymer support under the reaction conditions. Hence, using  $\text{Cu}(\text{OAc})_2$  as the source of copper, displacement of acetate would provide a copper-bound polymer-supported catalyst.

## 2. Experimental

Analytical grade reagents and freshly distilled solvents were used throughout. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by molecular sieve and solid substrates were recrystallized before use. Distillation, purification of the solvents and substrate were done by standard procedures [39]. 5.5% crosslinked chloromethylated polystyrene was purchased from Aldrich Chemical Company; U.S.A. Copper acetate was procured from Merck and used without further purification.

The FT-IR spectra of the samples were recorded from 400 to 4000  $\text{cm}^{-1}$  on a Perkin-Elmer FT-IR 783 spectrophotometer using KBr pellets. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). The reaction products were quantified (GC data) by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector and identified by Trace DSQ II GC-MS equipped with a 60 m TR-50MS capillary column.

### 2.1. General procedure for the *O*-arylation of phenol with aryl halides

Polymer supported Cu(II) catalyst (0.05 g, 0.0098 mmol) in DMSO (5 mL) was taken in a 100 mL R.B flask and stirred at room temperature for 10 min. Then aryl halide (1 mmol), phenol (1 mmol), tetrabutylammonium bromide ( $\text{tBu}_4\text{NBr}$ ) (0.1 mmol),  $\text{Cs}_2\text{CO}_3$  (1 mmol) and DMSO (5 mL) were added to it. The final reaction mixture was refluxed at 120 °C under an open air condition. The reaction mixtures were collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  by vacuum. The filtrate was concentrated by vacuum and the resulting residue was purified

by column chromatography on silica gel to provide the desired product.

### 2.2. General procedure for the *N*-arylation of *N*-H heterocycles with arylboronic acids

In a 100 mL RB flask, polymer supported Cu(II) catalyst (50 mg, 0.0098 mmol), arylboronic acid (1 mmol), *N*-H heterocycles (1.2 mmol), and 10 mL methanol were stirred under nitrogen atmosphere, at 40 °C. The reaction mixtures were collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  by vacuum. The filtrate was concentrated by vacuum and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

### 2.3. General procedure for the amination of aromatic amines with arylboronic acids

In a 100 mL RB flask, polymer supported Cu(II) catalyst (50 mg, 0.0098 mmol), arylboronic acid (1.5 mmol), aromatic amines (1.2 mmol),  $\text{K}_2\text{CO}_3$  (1 mmol), and 10 mL DMSO stirred under nitrogen atmosphere, at 140 °C. The reaction mixtures were collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  by vacuum. The filtrate was concentrated by vacuum and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

### 2.4. General procedure for the amination of aromatic amines with aryl halides

In an oven dried 100 mL RB flask, polymer supported Cu(II) catalyst (50 mg, 0.0098 mmol), aryl halide (1 mmol), aromatic amines (1.2 mmol), KOH (1 mmol), and 10 mL DMSO were stirred under nitrogen atmosphere, at 140 °C. The reaction mixtures were collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  by vacuum. The filtrate was concentrated by vacuum and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

### 2.5. Synthesis of the metal complexes

The preparation procedure followed to obtain the catalyst is given in Scheme 1. Catalyst was readily prepared in two steps. Firstly, the 2 g of chloromethylated polystyrene copolymer (**2**) treated with 0.979 g of  $\beta$ -alanine (**1**) to produce corresponding polymer anchored ligand in the presence of sodium carbonate base (0.759 g) in *N,N*-dimethylformamide solvent (DMF) at 100 °C for 48 h to obtain a light brown polymer (**L**). The polymer was washed thoroughly with DMF to remove excess  $\beta$ -alanine and then with 1 M HCl to remove excess base. Finally, it was washed with double distilled water, dried and stored at room temperature for further use. This Polymer anchored  $\beta$ -alanine ligand (1 g) in acetic acid (20 mL) was treated with 5 mL 1% (w/v) acetic acid solution of

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